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**PATENT**  
Attorney Docket  
No.: **C 2572 COGG**

#### **TITLE OF THE INVENTION**

**Methods of Coating Glass Using Water-Dispersible Epoxy Resin Compositions,  
Glass Materials Coated Therewith and Composite Materials Containing the Same**

#### **BACKGROUND OF THE INVENTION**

5   **[0001]**       European Patent Publication No. 0137427A describes sizing  
preparations for glass fibers consisting essentially of coupling agents, film formers  
and optionally lubricants, wetting agents and other additives known per se. The  
sizes additionally contain water-insoluble or water-dispersible masked  
polyisocyanates.

#### 10                   **SUMMARY OF THE INVENTION**

**[0002]**       The problem addressed by the present invention was to provide  
substances or compositions which would be suitable for coating glass and especially  
glass fibers.

**[0003]**       The present invention relates to the use of water-dispersible epoxy  
15   resins solid at 20°C excluding reaction products of bisphenol A and/or bisphenol F  
with epichlorohydrin for coating glass.

**[0004]**       The present invention also relates to the use of aqueous two-  
component coating compositions containing

20   A)     1 to 98% by weight water-dispersible epoxy resins solid at 20°C excluding  
reaction products of bisphenol A and/or bisphenol F with epichlorohydrin,

B) 1 to 98% by weight water-dilutable epoxy resin hardeners and

W) 1 to 98% by weight water

for coating glass. In one embodiment, the glass to be coated consists of glass fibers.

**[0005]** The present invention also relates to coated glass fibers obtainable by

5 contacting an aqueous two-component coating composition containing

A) 1 to 98% by weight water-dispersible epoxy resins solid at 20°C excluding  
reaction products of bisphenol A and/or bisphenol F with epichlorohydrin,

B) 1 to 98% by weight water-dilutable epoxy resin hardeners and

W) 1 to 98% by weight water

10 with the surface of the glass fibers and then curing the coating composition.

**[0006]** The present invention also relates to the use of coated glass fibers  
obtainable as just described for reinforcing synthetic fibers.

**[0007]** In another embodiment, the present invention relates to a composite  
material containing coated glass fibers obtainable as described above.

15 **[0008]** It is specifically pointed out that individual species or mixtures of  
such species may be used for components A) and B). In other words, both one and  
also several epoxy resins A) or epoxy resin hardeners B) may be used.

**[0009]** The percentages by weight mentioned for components A) and B) are  
always based on the respective active substance contents. If, for example, an

20 aqueous two-component coating composition is prepared by using one or more  
components in a water-based supply form, it is the quantity of active substance  
present in the individual components and not whether certain components were used  
in water-free or water-containing form in the production of the coating composition  
which is crucial to characterization of the composition of the two-component  
25 coating composition as a whole. Accordingly, the percentage content of component  
W), i.e. water, is always the sum total of water present in the coating composition as  
a whole.

## DETAILED DESCRIPTION OF THE INVENTION

### Component A)

[0010] Component A) of the coating compositions according to the invention is formed by water-dispersible epoxy resins solid at 20°C, reaction products of bisphenol A and/or bisphenol F with epichlorohydrin being excluded as component A).

[0011] Water-dispersible epoxy resins solid at 20°C which are self-dispersing in water are preferably used as component A). To the expert, "self-dispersing" means that the corresponding compounds lead spontaneously to the formation of dispersions or emulsions on contact with water without the assistance of special emulsifiers, dispersants or the like.

[0012] Examples of suitable compounds A) are the compounds formed by reaction of an epoxy resin with mono-, di- or polyalkyleneamines in accordance with WO-A-95/18165 or by reaction of an epoxy resin with polyhydric phenols and amine/epoxy adducts in accordance with WO-A-96/20970. The following compounds are also suitable for use as compounds A): intermediate product Z5 which is formed in the production of the type B2) hardeners according to the invention (see below), and intermediate product Z7 which is formed in the production of the type B3) hardeners according to the invention (see below).

[0013] Examples of commercially available compounds A) are the products Waterpox 1402, Waterpox 1422, Waterpox 1450 and Waterpox 1455 which can be obtained from Cognis Deutschland GmbH & Co. KG. All these products are available as water-containing supply forms.

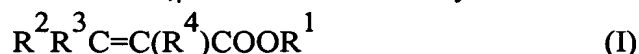
### Component B)

[0014] Component B) of the coating compositions according to the invention is a water-dilutable epoxy resin hardener. Compounds derived from adducts based on  $\alpha,\beta$ -unsaturated carboxylic acid esters and mono-, di- or polyaminopolyalkylene oxide compounds are preferably used as component B). The compounds B) are preferably selected from the group of types B1) to B3)

described hereinafter.

[0015] Hardeners of the B1) type are obtainable by:

(a) reacting one or more  $\alpha,\beta$ -unsaturated carboxylic acid esters (I)



5 where  $R^1$  is an aromatic or aliphatic radical containing up to 15 carbon atoms, the substituents  $R^2$ ,  $R^3$  and  $R^4$  independently of one another represent hydrogen, branched or unbranched, aliphatic or aromatic groups containing up to 20 carbon atoms or a group  $-(CH_2)_n-COOR^1$ , where  $R^1$  is as defined above and n is a number of 0 to 10, in the presence of a transesterification catalyst with

10 (b) one or more hydroxy compounds, compounds (a) and (b) being used in such quantities that the equivalent ratio of the hydroxyl groups in (b) to the ester groups  $COOR^1$  in the  $\alpha,\beta$ -unsaturated carboxylic acid esters (a) is in the range from 1.5:1 to 10:1;

reacting this intermediate product Z1 obtained with

15 (c) one or more mono-, di- or polyaminopolyalkylene oxide compounds, an equivalent ratio of the reactive hydrogen atoms at the aminonitrogen atoms of (c) to the ester groups in the intermediate compound Z1 in the range from 10:1 to 1:10 being adjusted;

subsequently reacting this intermediate product Z2 obtained with

20 (d) one or more polyepoxides, the equivalent ratio of oxirane rings in polyepoxide (d) to reactive hydrogen atoms of the mono-, di- or polyaminopolyalkylene oxide compounds used in (c) being adjusted to a value of 100:1 to 1.5:1,

and subsequently reacting this intermediate product Z3 obtained with

25 (e) one or more primary and/or secondary amines, the equivalent ratio of oxirane rings in the intermediate product Z3 to the reactive H atoms at the aminonitrogen atoms of (e) being adjusted to a value of 1:1.5 to 1:20.

[0016] The hardeners according to the invention are either liquid or solid substances, depending on their molecular weight.

30 [0017] The expression "equivalent ratio" is familiar to the expert. The basic concept behind the notion of the equivalent is that, for every substance participating

in a reaction, the reactive groups involved in the desired reaction are taken into consideration. By indicating an equivalent ratio, it is possible to express the ratio which all the various reactive groups of the compounds (x) and (y) used bear to one another. It is important in this connection to bear in mind that a reactive group is understood to be the smallest possible reactive group, i.e. the notion of the reactive group is not identical with the notion of the functional group. In the case of H-acid compounds, this means for example that, although OH groups or NH groups represent such reactive groups, NH<sub>2</sub> groups with two reactive H atoms positioned at the same nitrogen atom do not. In their case, the two hydrogen atoms within the functional group NH<sub>2</sub> are appropriately regarded as reactive groups so that the functional group NH<sub>2</sub> contains two reactive groups, namely the hydrogen atoms.

[0018] In one embodiment, the intermediate compound Z1 and the compound (c) are used in such quantities that the equivalent ratio of reactive hydrogen atoms at the aminonitrogen atoms of (c) to the ester groups in the intermediate compound Z1 is in the range from 4:1 to 1:4 and more particularly in the range from 2.5:1 to 1.5:1.

[0019] In another embodiment, the equivalent ratio of oxirane rings in the polyepoxide (d) to reactive hydrogen atoms of the mono-, di- or polyaminopolyalkylene oxide compounds used in (c) is adjusted to a value in the range from 50:1 to 10:1.

[0020] Examples of the  $\alpha,\beta$ -unsaturated carboxylic acid esters (a) corresponding to formula (I) to be used in accordance with the invention are methyl acrylate, ethyl acrylate, dimethyl maleate, diethyl maleate, dimethyl fumarate, diethyl fumarate, dimethyl itaconate, diethyl itaconate. Particularly preferred compounds (a) are dialkyl maleates, more particularly diethyl maleate and dimethyl maleate.

[0021] The hydroxy compounds (b) may be aliphatic or aromatic. The compounds (b) should be inert to transesterification catalysts. Examples of suitable aromatic compounds (b) are resorcinol, hydroquinone, 2,2-bis-(4-hydroxyphenyl)-propane (bisphenol A), isomer mixtures of dihydroxydiphenyl methane (bisphenol F), tetrabromobisphenol A, 4,4'-dihydroxydiphenyl

cyclohexane, 4,4'-dihydroxy-3,3-dimethyldiphenyl propane, 4,4'-dihydroxydiphenyl, 4,4'-dihydroxybenzophenol, bis-(4-hydroxyphenyl)-1,1-ethane, bis-(4-hydroxyphenyl)-1,1-isobutane, bis-(4-hydroxyphenyl)-methane, bis-(4-hydroxyphenyl)-ether, bis-(4-hydroxyphenyl)-sulfone etc. and the chlorination and bromination products of the above-mentioned compounds. Bisphenol A is the preferred aromatic compound (b).

**[0022]** In one preferred embodiment, the hydroxy compounds (b) are selected from the class of fatty alcohols, alkanediols and polyetherdiols. If desired, these compounds may also be alkoxylated.

10 **[0023]** The fatty alcohols are primary alcohols containing 6 to 36 carbon atoms which may be saturated or olefinically unsaturated. Examples of suitable fatty alcohols are hexanol, heptanol, octanol, pelargonyl alcohol, decanol, undecanol, lauryl alcohol, tridecanol, myristyl alcohol, pentadecanol, palmityl alcohol, heptadecanol, stearyl alcohol, nonadecanol, arachidyl alcohol, heneicosanol, behenyl alcohol, tricosanol, lignoceryl alcohol, 10-undecanol, oleyl alcohol, elaidyl alcohol, ricinolyl alcohol, linoleyl alcohol, linolenyl alcohol, gadoleyl alcohol, arachidonyl alcohol, erucyl alcohol, brassidyl alcohol.

15 **[0024]** The alkanediols are compounds corresponding to the general formula  $\text{HOCH}_2\text{-R}^5\text{-CH}_2\text{OH}$ , where  $\text{R}^5$  is a hydrophobic hydrocarbon radical which may be saturated or unsaturated, linear or branched and may also contain aromatic structural elements. Examples are hexane-1,6-diol, heptane-1,7-diol and octane-1,8-diol, polyoxytetramethylenediols - also known as polytetrahydrofurans - and the so-called dimerdiols. Dimer diols are most particularly preferred for the purposes of the present invention.

25 **[0025]** Dimerdiols are well-known commercially available compounds which are obtained, for example, by reduction of dimer fatty acid esters. The dimer fatty acids on which these dimer fatty acid esters are based are carboxylic acids which may be obtained by oligomerization of unsaturated carboxylic acids, generally fatty acids, such as oleic acid, linoleic acid, erucic acid and the like. The oligomerization is normally carried out at elevated temperature in the presence of a catalyst, for example of clay. The substances obtained - dimer fatty acids of

technical quality - are mixtures in which the dimerization products predominate. However, small amounts of higher oligomers, more particularly the trimer fatty acids, are also present. Dimer fatty acids are commercially available products and are marketed in various compositions and qualities. Abundant literature is available

5 on the subject of dimer fatty acids, cf. for example the following articles: Fette & Öle 26 (1994), pages 47-51; Speciality Chemicals 1984 (May Number), pages 17, 18, 22-24. Dimerdiols are well-known among experts, cf. for example a more recent article in which inter alia the production, structure and chemistry of the dimerdiols are discussed: Fat Sci. Technol. 95 (1993), No. 3, pages 91-94.

10 According to the invention, preferred dimerdiols are those which have a dimer content of at least 50% and more particularly 75% and in which the number of carbon atoms per dimer molecule is mainly in the range from 36 to 44.

[0026] Polyetherdiols in the context of the present invention are diols corresponding to the general formula  $\text{HOCH}_2\text{-R}^6\text{-CH}_2\text{OH}$ , where  $\text{R}^6$  is a

15 hydrophobic hydrocarbon radical which may be saturated or unsaturated, linear or branched and may also contain aromatic structural elements and in which one or more  $\text{CH}_2$  units must each be replaced by an oxygen atom.

[0027] A particularly attractive class of polyetherdiols can be obtained by alkoxylation of alkanediols, such as ethane-1,2-diol, propane-1,3-diol, propane-1,2-

20 diol, butane-1,4-diol, butane-1,3-diol, pentane-1,5-diol, hexane-1,6-diol, heptane-1,7-diol and octane-1,8-diol, polyoxytetramethylenediols (polytetrahydrofurans) and dimerdiols. The production of these alkoxyated diols is normally carried out as follows: in a first step, the required diol is contacted with ethylene oxide and/or propylene oxide and the resulting mixture is reacted in the presence of an alkaline

25 catalyst at temperatures of 20 to 200°C. Addition products of ethylene oxide (EO) and/or propylene oxide (PO) onto the diol used are obtained in this way. The addition products are therefore EO adducts or PO adducts or EO/PO adducts with the particular diol; in the case of the EO/PO adducts, the addition of EO and PO may take place statistically or blockwise.

30 [0028] Suitable transesterification catalysts for the reaction of the compounds (a) and (b) are any transesterification catalysts known to the expert from

the prior art. Examples of suitable catalysts are sodium methyllate, dibutyl tin diacetate, tetraisopropyl orthotitanate. If desired, the catalysts may be deactivated after the transesterification although this is not absolutely essential.

[0029] Suitable amino components (c) are mono-, di- or

5 polyaminopolyalkylene oxide compounds. By this is meant that these compounds contain, on the one hand, one two or more amino functions (NH or NH<sub>2</sub> functions) and, on the other hand, alkylene oxide units. The alkylene oxide units are, in particular, ethylene oxide, propylene oxide and butylene oxide, ethylene oxide and propylene oxide being particularly preferred. The compounds (c) are substances at  
10 least partly soluble in water at 20°C.

[0030] The production of the compounds (c) is known from the prior art and comprises the reaction of hydroxyfunctional compounds with alkylene oxides and subsequent conversion of the resulting terminal hydroxyl groups into amino groups.

[0031] So far as the reaction of hydroxyfunctional compounds with alkylene  
15 oxides is concerned, ethoxylation and propoxylation are of particular importance. The following procedure is usually adopted: in a first step, the required hydroxyfunctional compounds are contacted with ethylene oxide and/or propylene oxide and the resulting mixture is reacted in the presence of an alkaline catalyst at temperatures in the range from 20 to 200°C. Addition products of ethylene oxide  
20 (EO) and/or propylene oxide (PO) are obtained in this way. The addition products are preferably EO adducts or PO adducts or EO/PO adducts with the particular hydroxyfunctional compound. In the case of the EO/PO adducts, the addition of EO and PO may be carried out statistically or blockwise.

[0032] In one embodiment, substances with the general formula  $R^8-O-R^9-CH_2CH(R^{10})-NH_2$  are used as the compounds (c). In this formula: R<sup>8</sup> is a  
25 monofunctional organic group containing 1 to 12 carbon atoms which may be aliphatic, cycloaliphatic or aromatic; R<sup>9</sup> is a polyoxyalkylene group made up of 5 to 200 polyoxyalkylene units, more particularly EO and/or PO units; R<sup>10</sup> is hydrogen or an aliphatic radical containing up to 4 carbon atoms.

30 [0033] Particularly suitable representatives of the compounds (c) for the purposes of the present invention are the "Jeffamines" known to the expert which

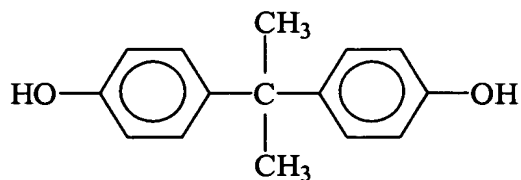


are commercially available substances. One example is "Jeffamine 2070" which, according to the manufacturer Texaco, is produced by reacting methanol with ethylene oxide and propylene oxide and then converting the terminal hydroxyl groups of the intermediate product initially obtained into amine groups (cf. WO 96/20971, page 10, lines 12-15).

[0034] The compounds (c) preferably have average molecular weights (number average Mn) of 148 to 5,000 and more particularly in the range from 400 to 2,000.

[0035] The epoxy compounds (d) are polyepoxides containing on average at least two epoxy groups per molecule. These epoxy compounds may be both saturated and unsaturated and aliphatic, cycloaliphatic, aromatic and heterocyclic and may also contain hydroxyl groups. They may also contain substituents which do not cause any troublesome secondary reactions under the mixing and reaction conditions, for example alkyl or aryl substituents, ether groups and the like. These epoxy compounds are preferably polyglycidyl ethers based on polyhydric, preferably dihydric, alcohols, phenols, hydrogenation products of these phenols and/or novolaks (reaction products of mono- or polyhydric phenols with aldehydes, more particularly formaldehyde, in the presence of acidic catalysts). The epoxy equivalent weights of these epoxy compounds are preferably between 160 and 500 and more preferably between 170 and 250. The epoxy equivalent weight of a substance is the quantity of the substance (in grams) which contains 1 mole of oxirane rings. Preferred polyhydric phenols are the following compounds: resorcinol, hydroquinone, 2,2-bis-(4-hydroxyphenyl)-propane (bisphenol A), isomer mixtures of dihydroxydiphenyl methane (bisphenol F), tetrabromobisphenol A, 4,4'-dihydroxydiphenyl cyclohexane, 4,4'-dihydroxy-3,3-dimethyldiphenyl propane, 4,4'-dihydroxydiphenyl, 4,4'-dihydroxybenzophenol, bis-(4-hydroxyphenyl)-1,1-ethane, bis-(4-hydroxyphenyl)-1,1-isobutane, bis-(4-hydroxyphenyl)-methane, bis-(4-hydroxyphenyl)-ether, bis-(4-hydroxyphenyl)-sulfone etc. and the chlorination and bromination products of the above-mentioned compounds. Bisphenol A is most particularly preferred.

### Bisphenol A



- 5    **[0036]**        The polyglycidyl ethers of polyhydric alcohols are also suitable compounds (d). Examples of such polyhydric alcohols are ethylene glycol, diethylene glycol, triethylene glycol, 1,2-propylene glycol, polyoxypropylene glycols ( $n = 1 - 20$ ), 1,3-propylene glycol, 1,4-butylene glycol, pentane-1,5-diol, hexane-1,6-diol, hexane-1,2,6-triol, glycerol and bis-(4-hydroxycyclohexyl)-2,2-
- 10    propane.
- [0037]**        Other suitable compounds (d) are polyglycidyl ethers of polycarboxylic acids obtained by reaction of epichlorohydrin or similar epoxy compounds with an aliphatic, cycloaliphatic or aromatic polycarboxylic acid, such as oxalic acid, succinic acid, adipic acid, glutaric acid, phthalic acid, terephthalic
- 15    acid, hexahydrophthalic acid, 2,6-naphthalenedicarboxylic acid and dimerized linolenic acid. Examples are adipic acid diglycidyl ester, phthalic acid diglycidyl ester and hexahydrophthalic acid diglycidyl ester.
- [0038]**        A comprehensive list of suitable epoxy compounds (d) can be found in: A.M. Paquin, "Epoxidverbindungen und Epoxidharze", Springer-Verlag, Berlin
- 20    1958, Chapter V, pages 308 to 461 and Lee, Neville "Handbook of Epoxy Resins" 1967, Chapter 2, pages 201 and 2-33.
- [0039]**        Mixtures of several epoxy compounds (d) may also be used.
- [0040]**        Amines (e) suitable for the purposes of the invention are primary and/or secondary amines. Preferred amines (e) are polyamines containing at least
- 25    two nitrogen atoms and at least two active aminohydrogen atoms per molecule. Aliphatic, aromatic, aliphatic-aromatic, cycloaliphatic and heterocyclic di- and polyamines may be used.
- [0041]**        The following are examples of suitable amines (e): polyethylene amines (ethylene diamine, diethylene triamine, triethylene tetramine, tetraethylene
- 30    pentamine, etc.), 1,2-propylene diamine, 1,3-propylene diamine, 1,4-butane diamine, 1,5-pentane diamine, 1,3-pentane diamine, 1,6-hexane diamine, 3,3,5-

trimethyl-1,6-hexanediamine, 3,5,5-trimethyl-1,6-hexane diamine, 2-methyl-1,5-pentane diamine, bis-(3-aminopropyl)-amine, N,N'-bis-(3-aminopropyl)-1,2-ethane diamine, N-(3-aminopropyl)-1,2-ethane diamine, 1,2-diaminocyclohexane, 1,3-diaminocyclohexane, 1,4-diaminocyclohexane, aminoethyl piperazines, the

5 poly(alkylene oxide)diamines and triamines (such as, for example, Jeffamine D-230, Jeffamine D-400, Jeffamine D-2000, Jeffamine D-4000, Jeffamine T-403, Jeffamine EDR-148, Jeffamine EDR-192, Jeffamine C-346, Jeffamine ED-600, Jeffamine ED-900, Jeffamine ED-2001), meta-xylylene diamine, phenylene diamine, 4,4'-diaminodiphenyl methane, toluene diamine, isophorone diamine, 3,3'-dimethyl-

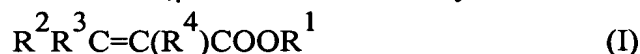
10 4,4'-diaminodicyclohexyl methane, 4,4'-diaminodicyclohexylmethane, 2,4'-diaminodicyclohexyl methane, the mixture of poly(cyclohexylaromatic)amines attached by a methylene bridge (also known as MBPCAA) and polyaminoamides.

[0042] Other suitable compounds (e) are the reaction products of the amines just mentioned with the above-described  $\alpha,\beta$ -unsaturated carboxylic acid esters (a)

15 and the reaction products of the amines just mentioned with the above-described polyepoxy compounds (d).

[0043] Hardeners of the B2) type are obtainable by:

(a) reacting one or more  $\alpha,\beta$ -unsaturated carboxylic acid esters (I):



20 where  $R^1$  is an aromatic or aliphatic radical containing up to 15 carbon atoms, the substituents  $R^2$ ,  $R^3$  and  $R^4$  independently of one another represent hydrogen, branched or unbranched, aliphatic or aromatic groups containing up to 20 carbon atoms or a group  $-(CH_2)_n-COOR^1$ , where  $R^1$  is as defined above and n is a number of 0 to 10, with

25 (c) one or more mono-, di- or polyaminopolyalkylene oxide compounds, compounds (a) and (c) being used in such quantities that the equivalent ratio of the reactive hydrogen atoms at the aminonitrogen atoms of (c) to the C=C double bond in the  $\alpha,\beta$ -position to the group  $COOR^1$  shown in formula (I) in the carboxylic acid esters (a) is in the range from 10:1 to 1:10;

30 subsequently reacting this intermediate product Z4 obtained with

(d) one or more polyepoxides, the equivalent ratio of oxirane rings in

polyepoxide (d) to reactive hydrogen atoms in the mono-, di- or polyaminopolyalkylene oxide compounds (c) being adjusted to a value of 100:1 to 1.5:1;

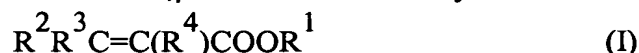
and subsequently reacting this intermediate product Z5 obtained with

- 5 (e) one or more primary and/or secondary amines, the equivalent ratio of oxirane rings in the intermediate product Z5 to the reactive H atoms at the aminonitrogen atoms of (e) being adjusted to a value of 1:1.5 to 1:20.

[0044] The foregoing observations on hardeners of the B1) type otherwise apply to the substances (a) and to the substances (c) to (e).

- 10 [0045] Hardeners of the B3) type are obtainable by:

- (a) reacting one or more  $\alpha,\beta$ -unsaturated carboxylic acid esters (I):



where  $\text{R}^1$  is an aromatic or aliphatic radical containing up to 15 carbon atoms, the substituents  $\text{R}^2$ ,  $\text{R}^3$  and  $\text{R}^4$  independently of one another represent hydrogen,

- 15 branched or unbranched, aliphatic or aromatic groups containing up to 20 carbon atoms or a group  $-(\text{CH}_2)_n-\text{COOR}^1$ , where  $\text{R}^1$  is as defined above and n is a number of 0 to 10, with;

- (c) one or more mono-, di- or polyaminopolyalkylene oxide compounds, compounds (a) and (c) being used in such quantities that the equivalent ratio of the reactive hydrogen atoms at the aminonitrogen atoms of (c) to the C=C double bond in the  $\alpha,\beta$ -position to the group  $\text{COOR}^1$  shown in formula (I) in the carboxylic acid esters (a) is in the range from 10:1 to 1:10,

subsequently reacting this intermediate product Z4 obtained with

- (g) one or more polyhydroxy compounds, the equivalent ratio of ester groups in the intermediate compound Z4 to hydroxy groups in the polyhydroxy compound (g) being adjusted to a value of 1:1.1 to 1:10,

and subsequently reacting this intermediate product Z6 obtained with

- (d) one or more polyepoxides, the equivalent ratio of oxirane rings in polyepoxide (d) to hydroxyl groups in the intermediate product Z6 being adjusted to a value of 1.5:1 to 6:1,

and subsequently reacting this intermediate product Z7 obtained with

(e) one or more primary and/or secondary amines, the equivalent ratio of oxirane rings in the intermediate product Z7 to the reactive H atoms at the aminonitrogen atoms of (e) being adjusted to a value of 1:1.5 to 1:20.

[0046] The foregoing observations on hardeners of the B1) type otherwise  
5 apply to the substances (a) and to the substances (c) to (e).

[0047] The polyhydroxy compounds (g) may be aliphatic or aromatic. In one embodiment, the polyhydroxy compounds (g) are selected from the class of special aliphatic diols, namely alkanediols, especially dimer diols, polyether diols and polyester diols. The foregoing observations on hardeners of the B1) type in  
10 relation to component (b) apply to the alkanediols, including the dimerdiols, and the polyether diols. Polyesterdiols in the context of the invention are diols corresponding to the general formula  $\text{HOCH}_2\text{-R}^7\text{-CH}_2\text{OH}$ , where  $\text{R}^7$  is a hydrophobic hydrocarbon radical which may be saturated or unsaturated, linear or branched and may also contain aromatic structural elements and in which one or  
15 more  $\text{CH}_2$  units must each be replaced by a COO unit. They are normally produced by reacting difunctional polyols with dicarboxylic acids or anhydrides thereof. Commonly used polyols are ethylene glycol, propane-1,2-diol, butane-1,4-diol, hexane-1,6-diol. Typical dicarboxylic acids are succinic acid, adipic acid, phthalic anhydride. Hexane-1,6-diol adipic acid polyesters are particularly preferred.

## 20 Other components

[0048] Besides the compulsory components A), B) and W) already mentioned, other additives may also be used – if desired – in the two-component coating compositions according to the invention. Examples of such additives include lubricants, plasticizers, antistatic agents, coupling agents, fillers, wetting  
25 agents and defoamers. In this case, the proviso applies that the sum total of all components of the two-component coating compositions, i.e. the sum of components A), B), W) and the other additives required, should come to 100% by weight.

## EXAMPLES

### Substances Used:

#### [0049] Epoxy Resins According to the Invention

Waterepoxy 1422: 100 parts contain 54 parts by weight solid epoxy resin, 36 parts  
5 by weight water and 10 parts by weight ethoxypropanol; epoxy equivalent = 1160  
(Cognis Deutschland GmbH & Co. KG/Germany).

Waterepoxy 1455: 100 parts contain 56 parts by weight solid epoxy resin, 37 parts  
by weight water and 7 parts by weight ethoxypropanol (Cognis Deutschland GmbH  
& Co. KG/Germany).

#### 10 [0050] Hardeners

Waterepoxy 751: amine-based hardener for epoxy resins (Cognis Deutschland  
GmbH & Co. KG/Germany).

Waterepoxy 603: polyamidoamine-based hardener for epoxy resins; 100 parts  
contain 50 parts by weight hardener and 50 parts by weight water; amine equivalent  
15 = 190 (Cognis Deutschland GmbH & Co. KG/Germany).

Waterepoxy 801: amine-based hardener for epoxy resins; 100 parts contain 60 parts  
by weight hardener, 35 parts by weight water and 5 parts by weight propylene  
glycol methyl ether; amine equivalent = 375 (Cognis Deutschland GmbH & Co.  
KG/Germany).

#### 20 Testing of Peel Strength

(to ISO 7004/DIN 53539)

[0051] Glass test specimens measuring 25 x 66 x 3 mm were degreased with  
acetone and dried. The test specimens were then coated on one surface with a  
mixture of epoxy resin and hardener using a film drawing knife (type 360,  
25 Erichsen/Sundwig). The coating thickness was 25 micrometers. The two  
components (epoxy resin and hardener) of the above-mentioned mixture were  
present in the exact stoichiometric mixing ratio, i.e. an equivalent ratio of 1:1.

[0052] After curing for 24 hours at 23°C, a commercially available two-  
component epoxy resin adhesive (Metallon FL, a product of Henkel KGaA,  
30 Düsseldorf) was applied to the coating of the glass test specimens. A strip of cloth  
(material: Mantelpopeline, polyester/cotton (67:33) blend; size of the strip: 25 x 195

mm) was then placed on the adhesive and held in place with clips. The test specimen thus prepared was then left for 7 days at 23°C, after which peel strength in N/mm<sup>2</sup> was determined by peeling off the strip of cloth using a Zwick tensile testing machine.

- 5 [0053] The results of the various tests are set out in Table 1. The peel strengths shown are the averages of three measurements.

Table 1

Resin	Hardener	Peel strength in N/mm <sup>2</sup>
Waterpoxy 1455	Waterpoxy 751	0.55
Waterpoxy 1455	Waterpoxy 603	1.03
Waterpoxy 1455	Waterpoxy 801	0.83
Waterpoxy 1422	Waterpoxy 751	1.39
Waterpoxy 1422	Waterpoxy 603	3.02
Waterpoxy 1422	Waterpoxy 801	2.96

- [0054] It will be appreciated by those skilled in the art that changes could be made to the embodiments described above without departing from the broad
- 10 inventive concept thereof. It is understood, therefore, that this invention is not limited to the particular embodiments disclosed, but it is intended to cover modifications within the spirit and scope of the present invention as defined by the appended claims.